ORGANIC ELECTROLUMINESCENT COMPONENT

The invention is directed to an organic electroluminescent component, particularly an organic light-emitting diode.

The visualization of data is constantly increasing in significance due to the

5   great increase in the amount of information. The technology of flat picture screens ("flat panel displays") was developed therefor for employment in mobile and portable electronic devices. The market of flat panel displays is currently largely dominated by the technology of liquid crystal displays (LC displays). In addition to cost-beneficial manufacture, low electrical power consumption, low weight and slight space

10   requirement, however, the technology of LC displays also exhibits serious disadvantages.

LC displays are not self-emitting and can therefore only be easily read or recognized given especially beneficial ambient light conditions. This makes a back-illumination device necessary in most instances, but this multiplies the thickness of

15   the flat panel display. Moreover, the majority part of the electrical power consumption is then needed for the illumination, and a higher voltage is required for the operation of the lamps or fluorescent tubes; this is usually generated from batteries or accumulators with the assistance of "voltage-up converters". Other disadvantages are the highly limited observation angles of LC displays and the long switching times

20   of individual pixels, these typically lying at a few milliseconds and also being highly temperature-dependent. The delayed image build-up is considered extremely disturbing, for example, given utilization in means of conveyance or given video applications.

There are other flat panel display technologies in addition to LC displays,

25   for example the technology of flat display panel cathode ray tubes, of vacuum-fluorescence displays and of inorganic thin-film electroluminescent displays. These technologies, however, have either not yet achieved the required degree of technological maturity or -- due to high operating voltages or, respectively, high

manufacturing costs -- they are only conditionally suited for utilization in portable electronic devices.

Displays on the basis of organic light-emitting diodes (=OLEDs) do not exhibit said disadvantages. The necessity of a back-illumination is eliminated due to

5   the self-emissivity, as a result whereof the space requirement and the electrical power consumption are considerably reduced. The switching times lie at about one microsecond and are only slightly temperature-dependent, which enables employment for video applications. The reading angle amounts to nearly 180°, and polarization films as required given LC displays are eliminated, so that a greater brightness of the

10 display elements can be achieved. Further advantages are the employability of flexible and non-planar substrates as well as a simple and cost-beneficial manufacture.

The construction of organic light-emitting diodes typically ensues in the following way.

A transparent substrate, for example glass, is coated with a transparent

15 electrode (bottom electrode, anode), composed, for example, of indium tin oxide (ITO). Dependent on the application, the transparent electrode is then structured with the assistance of a photolithographic process.

One or more organic layers composed of polymers, oligomers, low-molecular compounds or mixtures thereof are applied on the substrate with the

20 structured electrode. Examples of polymers are polyaniline, poly(p-phenylene-vinylene) and poly(2-methoxy-5-(2'-ethyl)-hexyloxy-p-phenylene-vinylene). Examples of low-molecular compounds that preferably transport positive charge carriers are N,N'-bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (m-TPD), 4,4',4"-tris-(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (m-MTDATA) and 4,4',4"-

25 tris-(carbazole-9-yl)-triphenylamine (TCTA). Hydroxy-chinoline aluminum-III salt (Alq_3) that can be doped with suitable chromophores (chinacridone derivatives, aromatic hydrocarbons, etc.), for example, is employed as emitter. As warranted, additional substances that influence the electro-optical and the long-term properties, such as copper phthalocyanine, can be present. The application of polymers usually

30 ensues from the liquid phase with doctor blades or spin-coating; low-molecular and

oligomeric compounds are usually deposited from the vapor phase by vapor deposition or "physical vapor deposition" (PVD). The overall layer thickness can amount to between 10 nm and 10 μm; it typically lies in the range between 50 and 200 nm.

5   A cooperating electrode (top electrode, cathode), which is usually composed of a metal, of a metal alloy or of a thin insulator layer and a thick metal layer, is applied onto the organic layer or layers. The manufacture of the cathode layer usually ensues with vapor phase deposition by means of thermal evaporation, electron beam evaporation or sputtering.

10   When metals are employed as cathode material, then these must have a low work function (typically < 3.7 eV) so that electrons can be efficiently injected into the organic semiconductor. Alkaline metals, alkaline earth metals or rare earth metals are usually employed for this purpose; the layer thickness lies between 0.2 nm and a few hundred nanometers but generally at a few 10 nanometers. Since, however, these

15   non-precious metals tend toward corrosion under atmospheric conditions, it is necessary to additionally apply a layer of a more precious, inert metal such as aluminum (Al), copper (Cu), silver (Ag) or gold (Au) onto the cathode layer that protects the non-precious metal layer against moisture and atmospheric oxygen.

         For increasing the stability of the cathodes against a corrosion-caused hole

20   formation, an alloy composed of an efficiently electron-injecting but corrosion-susceptible non-precious metal (work function < 3.7 eV) and a corrosion-resistant precious metal, such as Al, Cu, Ag and Au, is often employed instead of an unalloyed non-precious metal. The proportion of the non-precious metal in the alloy can amount to between a few tenths of a percent and approximately 90%. The alloys are usually

25   generated by simultaneous deposition of the metals from the vapor phase, for example by co-vapor deposition, simultaneous sputtering with a plurality of sources and sputtering upon employment of alloy targets. However, a layer of precious metal, such as Al, Cu, Ag or Au, is usually also additionally applied onto such cathodes as protection against corrosion.

Cathodes composed of precious metals, i.e. metals having a work function > 3.7 eV, are very inefficient electron injectors when they are utilized in direct contact with the organic semiconductor. When, however, a thin insulating intermediate layer (layer thickness generally between 0.2 and 5 nm) is arranged between the uppermost,

5 electron-conducting organic layer and the metal electrode, then the efficiency of the light-emitting diodes rises substantially. Oxides such as aluminum oxide, alkaline and alkaline earth oxides and other oxides as well as alkaline and alkaline earth fluorides come into consideration as insulating material for such an intermediate layer (in this respect, see Appl. Phys. Lett., Vol. 71 (1997), pages 2560 through 2562;

10 United States Letters Patent 5,677,572; European Published Application 0 822 603). A metal electrode that is composed of a pure metal or of a metal alloy is then applied onto the thin, insulating intermediate layer. The insulating material can thereby also be applied together with the electrode material by means of co-vapor deposition (Appl. Phys. Lett., Vol. 73 (1998), pages 1185 through 1187).

15 An object of the invention is to fashion an organic electroluminescent component, particularly an organic light-emitting diode, such that, on the one hand, a hermetic seal of the top electrode can be foregone and, on the other hand, the selection of materials employable at the cathode side is greater.

This is inventively achieved by a component that is characterized by

20 -- a transparent bottom electrode situated on a substrate;

-- a top electrode composed of a metal that is inert to oxygen and moisture;

-- at least one organic function layer arranged between the bottom electrode and the top electrode; and

-- a charge carrier injection layer containing a complex metal salt of the

25 composition $(Me1)\,(Me2)F_{m+n}$, whereby the following applies:

m and n are respectively a whole number corresponding to the valence of the metals Me1 and Me2 (the metal Me1 thereby has the valence m, the metal Me2 the valence n),

Me1 = Li, Na, K, Mg or Ca,

Me2 = Mg, Al, Ca, Zn, Ag, Sb, Ba, Sm or Yb,

with the prescription: Me1 ≠ Me2.

The critical feature of the organic electroluminescent component of the invention is thus comprised in a specific structure at the cathode side, namely in the

5   combination of a top electrode that is indifferent with respect to environmental influences with a charge carrier injection layer composed of a specific complex metal salt having the composition (Me1) (Me2)F_{m+n}, i.e. a double fluoride. As a result of this structure, a hermetic seal or, respectively, sealing of the top electrode can be omitted. As a result of the specific material for the charge carrier injection layer, not

10   only is the offering for the materials employable at the cathode side broadened, this material also achieves an improvement of the emission properties, expressed in a clearly higher light yield, a reduced operating voltage and a longer service life during operation.

The charge carrier injection layer (composed of a specific complex metal

15   salt) is preferably arranged as a thin insulating layer between the top electrode and the organic function layer, between the uppermost function layer and the top electrode given the presence of a plurality of function layers. When an electron transport layer is also additionally located on the (uppermost) function layer given the component of the invention, then the charge carrier injection layer is arranged between this layer and

20   the top electrode. In all of these instances, the thickness of the charge carrier injection layer preferably amounts to approximately 0.1 through 20 nm.

However, the charge carrier injection layer can also be quasi-integrated into the top electrode, into the (uppermost) organic function layer or into an electron transport layer that is potentially present, i.e. the complex metal salt is then a

25   constituent part of one of said layers. The production of such layers can advantageously ensue by means of co-vapor deposition of the corresponding materials, for example by co-vapor deposition of the top electrode material and of the complex metal salt.

The complex metal salt exhibits the composition (Me1) (Me2)F_{m+n}, whereby m and n correspond to the valence of the respective metal. m = 1 (Li, Na, K) or m = 2 (Mg, Ca) is valid for Me1; n = 1 (Ag) or n = 2 (Mg, Ca, Zn, Ba) or n = 3 (Al, Sb, Sm, Yb) is valid for Me2. The metal Me1 is preferably lithium (Li); the metal Me2 is preferably magnesium (Mg), aluminum (Al), calcium (Ca), silver (Ag) or Barium (Ba).

Advantageously, one of the double fluorides $LiAgF_2$, $LiBaF_3$ and $LiAlF_4$ is employed as complex metal salt. More such double fluorides are, for example, $NaAgF_2$, $KAgF_2$, $LiMgF_3$, $LiCaF_3$, $CaAgF_3$ and $MgBaF_4$. Complex salts of this type as well as methods for manufacturing them are known in and of themselves (in this respect, see the exemplary embodiments as well as, for example, "Gmelins Handbuch der Anorganischen Chemie", 8th Edition (1926), System Number 5 (fluorine), pages 58 through 72).

The top electrode, which generally comprises a thickness > 100 nm, is preferably composed of one of the following metals: aluminum (Al), silver (Ag), platinum (Pt) and gold (Au). The electrode material, however, can also be an alloy of two of these metals. Magnesium (Mg), calcium (Ca), zinc (Zn), antimony (Sb) and barium (Ba) come into consideration as further metals for the top electrode.

The bottom electrode is generally composed of indium tin oxide (ITO). Further possible materials for the bottom electrode are tin oxide and bismuth oxide. Glass generally serves as substrate for the bottom electrode.

The component of the invention preferably comprises two organic function layers, namely an apertured conducting layer arranged at the bottom electrode that transports positive charge carriers and an emission layer situated thereon that is also referred to as luminescence layer. Two or more apertured conducting layers can also be advantageously utilized instead of one apertured conducting layer.

The materials for said layers are known in and of themselves. In the present case, N,N'-bis-(3-methylphenyl)-N,N'-bis(phenyl)-benzidine (m-TPD), 4,4',4"-tris-(N-1-naphthyl-N-phenylamino)-triphenylamine (naphdata) or N,N'-bis-phenyl-N,N'-bis-α-naphthyl-benzidine (α-NPD) is preferably employed for the

apertured conducting layer or layers. The material for the emission layer is preferably hydroxychinoline aluminum-III salt (Alq_3). Simultaneously, this material can also serve for the electron transport. For example, chinacridone can also be utilized for the emission layer, one of the oxadiazole derivatives known for this purpose for a

5   potentially present electron transport layer.

The invention offers the following, further advantages, particularly in view of organic light-emitting diodes:

--   Facilitated Handling

Due to the stability of the material of the top electrode, work need not be

10   carried out under an inert gas atmosphere in the manufacture and further-processing of OLEDs.

--   Performance

Compared to top electrodes of non-precious metals, the operating voltage is clearly lowered and the light yield and efficiency are considerably

15   enhanced.

--   Improved Properties

Compared, for example, to LiF as material for the intermediate layer, compounds such as $LiAlF_4$ have the advantage that they are less hygroscopic, which facilitates the handling and storage. The double

20   fluorides are also easier to evaporate and are less basic (than LiF), as a result whereof the compatibility with the organic function layers is increased.

The invention shall be explained in still greater detail on the basis of exemplary embodiments and Figures.

25   Shown are:

Figure 1   a traditional OLED display;

Figure 2   an OLED display of the invention;

Figure 3   luminance/voltage characteristics;

Figure 4   efficiency/luminance characteristics;

30   Figure 5   a comparison of the luminance of various materials.

Example 1

Production of lithium aluminum fluoride $LiAlF_4$

Lithium aluminum hydride $LiAlH_4$ is carefully hydrolyzed with distilled water; conversion is subsequently undertaken with hydrofluoric acid (HF) in excess.

5   The complex metal salt $LiAlF_4$ that thereby precipitates out is extracted, repeatedly washed with water and ethanol and then dried.

Example 2

Production of lithium silver fluoride $LiAgF_2$

A solution of stoichiometric quantities of lithium hydroxide and silver

10   acetate is glacial acetic acid is converted with hydrofluoric acid (HF) in excess upon exclusion of light; the complex metal salt $LiAgF_2$ thereby precipitates out. The complex salt is extracted after the addition of the same volume of ethanol, is washed with ethanol and dried.

Example 3

15   Production of lithium barium fluoride $LiBa_3$

An aqueous solution of stoichiometric quantities of lithium hydroxide and barium hydroxide is converted with hydrofluoric acid (HF) in excess. The complex metal salt $LiBaF_3$ precipitates out when chilled (cooling with ice); it is extracted, repeatedly washed with ethanol and then dried.

20   The complex metal salt $LiCaF_3$ is produced in a corresponding way, whereby the reaction solution is constricted as warranted.

The complex metal salt $LiMgF_3$ can be produced in the same way; lithium methylate and magnesium methylate are then utilized as initial substances.

Example 4

25   Manufacture of a traditional OLED display (10) with a Mg/Ag cathode (see Figure 1)

An ITO layer (12) having a thickness of approximately 100 nm is applied onto a glass substrate (11). This layer is then photolithographically structured in such a way that a stripe-shaped structure arises. A layer of m-TPD (13) having a thickness of approximately 100 nm is first applied by thermal evaporation onto the coated substrate pre-treated in this way, followed by a layer (14) of Alq_3 having a thickness of approximately 65 nm.

A layer (15) of a magnesium-silver alloy (Mg:Ag mixing ratio 10:1) having a thickness of approximately 150 nm is applied onto the organic layer (14) by thermal evaporation with two simultaneously operated evaporator sources, and a layer (16) of pure silver having a thickness of approximately 150 nm is applied on said layer (15), likewise by thermal evaporation. The metal layers are thereby vapor-deposited through a mask with stripe-shaped openings, so that cathode stripes that lie perpendicular to the ITO stripes arise. Organic light-emitting diodes with an active area of 2 x 2 mm^2 respectively arise in this way at the intersections of the ITO tracks with the metal tracks -- together with the organic layers lying therebetween. During operation, the ITO layer is positively contacted; the metal tracks are negatively contacted.

Example 5

Manufacture of an OLED display (20) of the invention (see Figure 2)

An ITO layer (22) having a thickness of approximately 100 nm is applied onto a glass substrate (21). This layer is then photolithographically structured in such a way that a stripe-shaped structure arises. A layer of m-TPD (23) having a thickness of approximately 100 nm is first applied by thermal evaporation onto the coated substrate pre-treated in this way, followed by a layer (24) of Alq_3 having a thickness of approximately 65 nm.

A layer (25) of $LiAlF_4$ having a thickness of approximately 1 nm is applied by thermal evaporation onto the organic layer (24), and a layer (26) of aluminum -- serving as top electrode -- having a thickness of approximately 150 nm is applied onto said layer (25), likewise by thermal evaporation. The two layers are

thereby vapor-deposited through a mask with stripe-shaped openings, corresponding to Example 4, so that organic light-emitting diodes arise. During operation, the ITO layer is positively contacted, the top electrode negatively.

The results of measurements at the OLEDs corresponding to Examples 4
5   and 5 are compiled in Table 1. The threshold voltage (of the electroluminescence), the voltage and the efficiency (respectively given a luminance of 1500 cd/m^2), the maximum luminance and the luminance given a current density of 50 mA/cm^2) are thereby recited as characteristic data.

Table 1

10

Example	Threshold voltage [V]	Voltage [V] at 1500 cd/m^3	Efficiency [lm/W] at 1500 cd/m^2	Maximum luminance [cd/m^2]	Luminance [cd/m^2] at 50 mA/cm^2
4	2.08	14.48	0.677	15957	1544
5	1.87	14.12	0.720	18801	1605

It can be seen that the threshold voltage and the operating voltage of the display of the invention (Example 5) lie below the corresponding values given the
15   traditional display (Example 4), even though the thickness of the LiAlF$_4$ was not optimized. The values for the efficiency and the luminances that are achieved given the display of the invention lie above the corresponding values of the traditional display.

Figure 3 shows the luminance/voltage characteristics of the displays
20   according to Examples 4 and 5. The increased luminance of the display of the invention can be clearly seem from this illustration.

The following can be stated overall:

--   The display of the invention (Example 5) employs a cathode of aluminum with which efficiencies are normally achieved that lie approximately 40 to
25   50% below the corresponding values given Mg/Ag cathodes (Example 4). Aluminum, on the other hand, is more stable than magnesium vis a vis environmental influences such as atmospheric oxygen and moisture.

--   Due to the introduction of a thin $LiAlF_4$ between the organic function layers and the Al cathode, however, the efficiency of OLEDs having an Al cathode can be increased, namely even above the corresponding values of OLEDs with Mg/Ag cathode. In this way, high-efficiency OLEDs with

5   stable cathode can be constructed.

Example 6

Manufacture of an OLED display with a Mg/Ag cathode

An ITO layer having a thickness of approximately 100 nm is applied onto a glass substrate. This layer is then photolithographically structured in such a way

10   that a stripe-shaped structure arises. A layer of naphdata having a thickness of approximately 55 nm is first applied by thermal evaporation onto the coated substrate pre-treated in this way, followed by a layer of α-NPD having a thickness of approximately 5 nm, and, finally, a layer of Alq_3 having a thickness of approximately 65 nm.

15   A layer of a magnesium-silver alloy (Mg:Ag mixing ratio 10:1) having a thickness of approximately 150 nm is applied onto the uppermost organic layer (of Alq_3) by thermal evaporation with two simultaneously operated evaporator sources, and a layer of pure silver having a thickness of approximately 150 nm is applied on said uppermost organic layer, likewise by thermal evaporation. The metal layers are

20   thereby vapor-deposited through a mask with stripe-shaped openings, so that cathode stripes that lie perpendicular to the ITO stripes arise. Organic light-emitting diodes with an active area of 2 x 2 mm^2 respectively arise in this way at the intersections of the ITO tracks with the metal tracks -- together with the organic layers lying therebetween. During operation, the ITO layer is positively contacted; the metal

25   tracks are negatively contacted.

Example 7

Manufacture of an OLED display with an Al cathode

Corresponding to Example 6, a display having three organic function layers is constructed. A layer of aluminum having a thickness of 150 nm is then applied in a corresponding way by thermal evaporation onto the uppermost organic layer (of Alq_3).

Example 8

Manufacture of an OLED display with an Al cathode and an LiF intermediate layer

A display with three organic function layers is constructed corresponding to Example 6. A layer of LiF having a thickness of approximately 0.5 nm is then applied onto the uppermost organic layer (of Alq_3) by thermal evaporation, and a layer of aluminum having a thickness of approximately 150 nm is applied on said uppermost organic layer. The two layers are thereby vapor-deposited through a mask having stripe-shaped openings in conformity with Example 6, so that organic light-emitting diodes arise. During operation, the ITO layer is positively contacted, the Al cathode negatively.

Example 9

Manufacture of an OLED display with an Al cathode and a $LiAlF_4$ charge carrier injection layer

A display with three organic function layers is constructed corresponding to Example 8. A layer of $LiAlF_4$ having a thickness of approximately 0.5 nm is then applied by thermal evaporation onto the uppermost organic layer (of Alq_3), and a layer of aluminum -- serving as top electrode -- having a thickness of approximately 150 nm is applied onto said $LiAlF_4$ layer, likewise by thermal evaporation. The structuring and the contacting ensue in conformity with Example 8.

Example 10

Manufacture of an OLED display with an Al cathode and a $LiAgF_2$ charge carrier injection layer

A display with three organic function layers is constructed corresponding to Example 6. A layer of $LiAgF_2$ having a thickness of approximately 0.5 nm is then applied by thermal evaporation onto the uppermost organic layer (of Alq_3), and a layer of aluminum -- serving as top electrode -- having a thickness of approximately 150 nm is applied onto said $LiAlF_4$ layer, likewise by thermal evaporation. The structuring and the contacting ensue in conformity with Example 8.

Example 11

Manufacture of an OLED display with an Al cathode and a $LiBaF_3$ charge carrier injection layer

A display with three organic function layers is constructed corresponding to Example 6. A layer of $LiBaF_3$ having a thickness of approximately 0.5 nm is then applied by thermal evaporation onto the uppermost organic layer (of Alq_3), and a layer of aluminum -- serving as top electrode -- having a thickness of approximately 150 nm is applied onto said $LiAlF_4$ layer, likewise by thermal evaporation. The structuring and the contacting ensue in conformity with Example 8.

The results of measurements at the OLEDs corresponding to Examples 6 through 11 are compiled in Table 2. The threshold voltage (of the electroluminescence), the voltage and the efficiency (respectively given a luminance of 1500 cd/m^2), the maximum luminance and the luminance given a current density of 50 mA/cm^2) are thereby recited as characteristic data.

Table 2

Example	Threshold voltage [V]	Voltage [V] at 1500 cd/m³	Efficiency [lm/W] at 1500 cd/m²	Luminance [cd/m²] at 50 mA/cm²
6	3.19	9.96	1.08	1722
7	7.15	16.52	0.48	1275
8	3.17	9.47	1.19	1809
9	4.23	11.97	0.88	1684
10	3.49	10.86	1.00	1745
11	2.56	9.58	1.26	1948

It can be seen that the threshold voltages and the operating voltages of the displays of the invention (Examples 9 through 11) that comprise an Al cathode and a charge carrier injection layer composed of a complex metal salt are comparable to the values that are obtained given displays with a Mg/Ag cathode or, respectively, with an Al cathode and a LiF intermediate layer (Examples 6 and 8) and lie clearly below the corresponding values given a display with a pure Al cathode (Example 7). The displays of the invention are also comparable to the Mg/Ag and Al-LiF displays in view of the efficiency and the luminance, whereby a display with a LiBaF$_3$ charge carrier injection layer (Example 11), in particular, exhibits high values.

Figure 4 shows the efficiency/luminance characteristics of the Examples 6 through 11. In particular, the superior position of an Al-LiBaF$_3$ of the invention can be clearly seen from this illustration.

It can be stated overall that the efficiency of LEDs with an Al cathode can be boosted above the corresponding values of OLEDs with a Mg/Ag cathode by introducing thin layers of a complex metal salt such as LiAlF$_4$, LiAgF$_2$ and LiBaF$_3$ between the organic function layers and the cathode. High-efficiency OLEDS with stable contact can be constructed in this way.

The values for the luminance (given a current density of 50 mA/cm²) of the materials according to Examples 6 through 11 are compared to one another in Figure 5. The good results that can be achieved with the displays of the invention also derive therefrom.